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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 7th Interim	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Molecular Modelling of Silane Primers for Adhesive Joints and Composite Materials		5. TYPE OF REPORT & PERIOD COVERED 7th Interim. April 197-July 1997
7. AUTHOR(s) P M Hobbs A J Kinloch		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Mechanical Engineering Department Imperial College, Exhibition Rd., London, SW7 2BX, UK		8. CONTRACT OR GRANT NUMBER(s) N68171-95-C-0118 R00 7736-MS-01
11. CONTROLLING OFFICE NAME AND ADDRESS United States Army European Research Office		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 15th July 1997
		13. NUMBER OF PAGES 4
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
<div style="border: 1px solid black; padding: 5px; text-align: center;"> <b>DISTRIBUTION STATEMENT A</b>            Approved for public release            Distribution Unlimited         </div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A main aim of the present work is to use computational molecular dynamics (MD) modelling to study the adsorption of both short- and long-chained organosilane primers on different types of metal oxides. Of particular interest will be the verification of the predictions from the modelling, wherever possible, using the existing experimental data to be found in the literature.		

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## 1. INTRODUCTION

Organosilanes have been used for many years to improve the adhesion and resistance to water attack, of polymer/metal and polymer/ceramic interfaces [1-3]. These organosilanes possess the general chemical formula  $R'-Si(R)_3$  where  $R'$  is usually a short carbon chain containing some additional chemical functionality capable of reacting with the polymeric coating or adhesive. The group  $R$  is a hydrolysable end-group such as an ethoxy, methoxy or chloro group which can react with water present, either in the pretreatment solution or adsorbed on the surface of the substrate. This reaction forms silanol ( $Si-OH$ ) groups. The enhanced adhesion that the organosilanes primers can offer, compared to conventional polymeric coatings and adhesives, is generally considered [2] to be due to the silanol groups strongly interacting, either physically or chemically, with the surface of the substrate.

More recently, experimental work has been performed by Cave and Kinloch [4] who synthesised and studied the adhesion of organosilanes with long alkyl chains, which were adsorbed on an aluminium-oxide substrate from solution. They found that, if the hydrocarbon chain (i.e. the group  $R'$ ) was greater than about eighteen carbon atoms in length and was non-polar, then the silane molecules would form a self-assembling monolayer structure. Such orientated monolayers were found to exhibit good adhesion, and impart good resistance to debonding of the interface in the presence of water.

Most recently, molecular dynamics simulations have been undertaken [5-7] to model the conformation of adsorbed silane primers, and the nature of their interactions with the substrate. Further, some initial attempts have been made to predict the tendency for water to displace the adsorbed organosilane layer. Clearly, if such computational modelling methods could be developed and verified, they would enable the more rapid development of novel, and more effective, silane primers.

Thus, a main aim of the present work is to use computational molecular dynamics (MD) modelling to study the adsorption of both short- and long-chained organosilane primers on different types of metal oxides. Of particular interest will be the verification of the predictions from the modelling, wherever possible, using the existing experimental data to be found in the literature.

## 2. SUMMARY OF MAIN CONCLUSIONS TO DATE

The adhesion of a series of organosilanes adsorbed on different metal-oxide substrates have been modelled using a computational molecular dynamics (MD) approach. The silanes modelled were:

- (a) the fully hydrolysed version of  $\gamma$ -glycidoxypropyltrimethoxysilane (GPMS),
- (b) the fully hydrolysed version of  $\gamma$ -glycidoxydecyltrimethoxysilane (GDMS),
- (c) the fully hydrolysed version of  $\gamma$ -glycidoxyeicosyltrimethoxysilane (GEMS).

The substrates were corundum ( $\alpha\text{-Al}_2\text{O}_3$ ), an amorphous form of aluminium oxide (amorphous alumina,  $\text{Al}_2\text{O}_3$ ) and haematite ( $\text{Fe}_2\text{O}_3$ ).

The first systems to be studied highlighted the effects of the alkyl chain length incorporated into the organometallic silane. The results were found to in very good agreement with the previous experimental results of Cave and Kinloch [4]. For example, the work of these authors showed that the hydrocarbon chain length had to exceed about eighteen carbon atoms in order to obtain a self-assembling, and so an highly-ordered, silane layer. From the theoretical modelling results it was found that only the GEMS (with twenty carbon atoms in its hydrocarbon chain) gives a high degree of order, as revealed by the very low degree of scatter in the inclination angle. Further, the inclination angle measured by Cave and Kinloch [4] was about  $60^\circ$ , which is in good agreement with the values deduced from the present computational modelling studies. Finally, the interfacial interactions between the -OH group on the silane and the substrate surface have also been successfully modelled.

The second systems to be modelled studied the effects of varying the type of metal-oxide substrate. Firstly, for a given substrate, the values of the thermodynamic works of adhesion,  $W_A$ , were not greatly dependent upon the actual organosilane employed. Secondly, for any given silane, the values of  $W_A$  with respect to the different substrates were in the ranking order of:

amorphous alumina ( $\text{Al}_2\text{O}_3$ ) > corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) > haematite ( $\text{Fe}_2\text{O}_3$ )

This ranking is in agreement with previous work [5] where the adhesion of the hydrolysed GPMS was modelled and the interaction with the amorphous alumina found to be significantly greater than for haematite. However, the present authors know of no experimental work on this subject. Hence, this prediction from the computational modelling must remain an interesting observation, awaiting experimental evidence before any further comments may be offered. Thirdly, the closest atomic contacts between the organosilane primer and the substrate were deduced, and in all cases the shortest interfacial bonds were between the hydrogen atom in the hydroxyl group on the silane primer and the oxygen atom in the metal oxide surface, and this relatively strong interaction between the silanol group on the primer and the substrate surface agrees with the experimental results [1-3]. The actual interfacial bond distance generally correlated with the value of  $W_A$ , the higher the value of  $W_A$  then shorter the bond length for the closest contact. This is, of course, as would indeed be expected.

The third systems to be considered examined the effects of water on the stability of the organosilane/corundum interface. Our initial approach was to deduce values of the thermodynamic works of adhesion,  $W_{AL}$ , of the various interfaces in the presence of water. However, the values of  $W_{AL}$  were found to be very dependent upon the choice of the number of water molecules used in the MD calculations. Thus, an alternative approach was adopted where a system was directly modelled which consisted of the substrate surface covered with a layer of adsorbate molecules. Then a layer of water molecules was added. Next, an upper layer of 'capping' adsorbate molecules were added. In this layer the silane molecules are fixed, thus restricting the water molecules so that they cannot

completely escape from the system, i.e. we have a 'reservoir' of water molecules. The number of water molecules in the 'reservoir' was varied and the number which diffused down to the oxide surface and displaced the silane, or whatever adsorbate was modelled, were also ascertained. Also, the change in the interaction energies between the start and finish of the MD simulation was deduced. (Although, from this value, the thermodynamic work of adhesion,  $W_{AL}$ , of the interface in the presence of water cannot be deduced, since the individual values of the various thermodynamics work of adhesion are not known, of course.) However, the change in the value of the interaction energy did enable a ranking of the stability of the various interfaces in the presence of water molecules to be determined. The results from this model were found to be independent of the number of water molecules in the 'reservoir', and the rankings for the stability of the various interfaces were in excellent agreement with experimental observations.

Thus, we have developed, and verified, MD simulations of the adhesion acting across various organosilane/metal-oxide interfaces. We aim to employ these MD computational models to predict the adhesion characteristics of different types of novel organosilane primers, verifying wherever possible the results from the modelling studies by reference to experimental results. It is hoped that such computational modelling methods will enable the more rapid development of novel, and more effective, organometallic primers.

### **3. FUTURE WORK**

Below is a list of the planned work for the remainder of this present year, and for next year:

#### **3.1 Verification of Model**

1. In order to complete the verification of the model, we intend to compare our modelling results with the experimental data from Dr. R. Ravel at Liverpool University, UK (whose work is part of the TTCP-P3 programme and is sponsored by DRA (Farnborough), UK). She has been using infra-red techniques to examine the orientation of molecules on corundum surfaces.

#### **3.2 Dynamic Simulations of Water Displacing the Silane**

Using our dynamic simulation model we will examine the following:

1. The effect of changing the epoxy end-group on the silane to other end groups, e.g. diamino end-groups.
2. Run a comparison of long and short chain alkanes to examine whether the size of the molecule affects the diffusion of water to the surface.
3. Run the water displacement calculations using the dynamic simulation model for the other substrate surfaces (i.e. haematite and amorphous aluminium oxide).

4. Compare our predictions with the results from the TTCP-P3 sponsored silane programme.

### 3.3 Further Development of the Model

We will need to develop the model alongside the experimental results which will come from the TTCP-P3 programme of work. We intend to adapt the model in the following ways:

1. Make the model more realistic by introducing relaxation of the corundum surface, and partial charges at the surface.
2. Add hydrogen groups to the surface of the aluminium oxide, and examine the effects on the adhesion of the silane primers.
3. Look at systems with the silane chemically-bonded to the surface. We will need to develop a chemical bonding mechanism in order to achieve this goal.
4. Examine how multiple layers of GPMS, and other silane, molecules adsorb onto the substrate surface.
5. Again, compare the results from the modelling predictions to the results from the TTCP-P3 sponsored research programme on silanes.

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